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Sodium-Based Battery Development

U.S Department of Energy Office of Electricity
(OE) Energy Storage Peer Review

Washington, D.C., September 17-19, 2014

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Participants & Acknowledgements

Multi-institution Collaboration Between Industry, Universities, a National Laboratory, and Government

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DOE – Office of Electricity Delivery and Energy Reliability



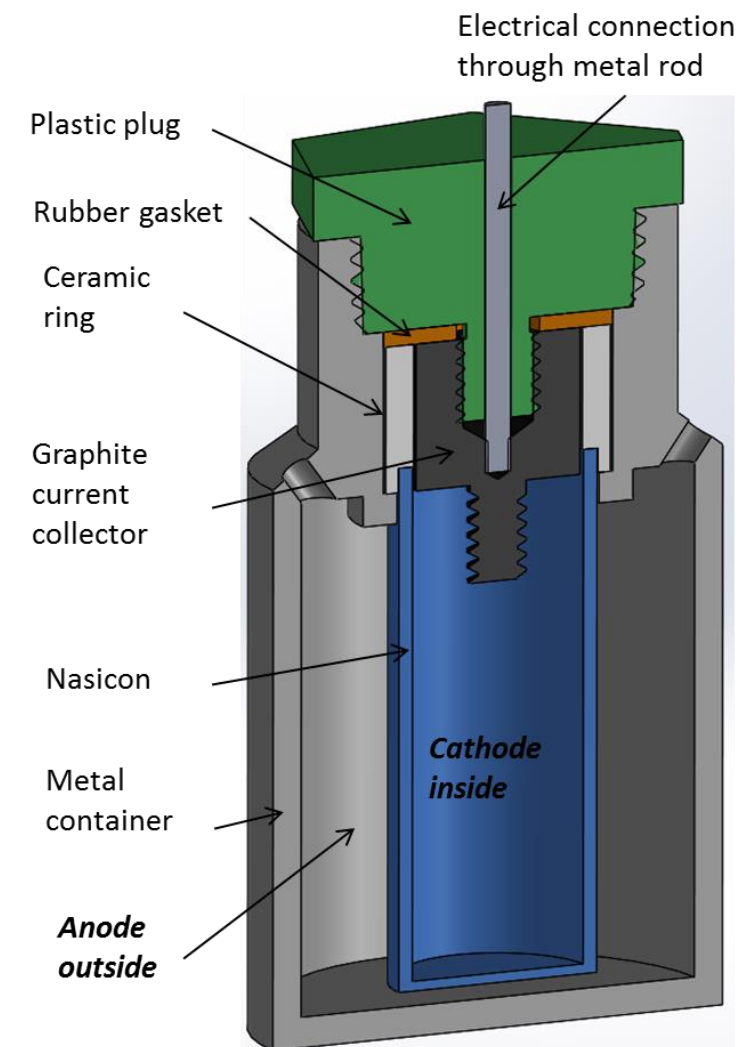
- Goal
 - reduce the cost of energy storage
 - cost of energy goal: < 100 \$/kWh
- Approach to low cost
 1. Develop new battery chemistries predicated on the use of widely available materials
 - low cost materials free of geopolitical constraints
 - Sodium metal as the anode – high energy density, low cost, widely available
 - low cost cathodes – bromine, iodine, air, etc
 2. Reduce/eliminate system inefficiencies
 - Use NaSICON as a solid ceramic separator which is a good sodium-ion conductor, is stable in direct contact with molten sodium, and will eliminate crossover.
 - Lower the operational temperature
 3. “Low” operational temperature allows use of low cost engineering materials for cell – e.g. plastics
- FY14 Focus Area – continue development of the sodium-halogen system
 - Continued to increase cell size, continue to improve materials performance, develop a conceptual cell design for a large-scale battery, develop a cost basis, begin evaluation and demonstration of the safety basis

Cell Chemistry

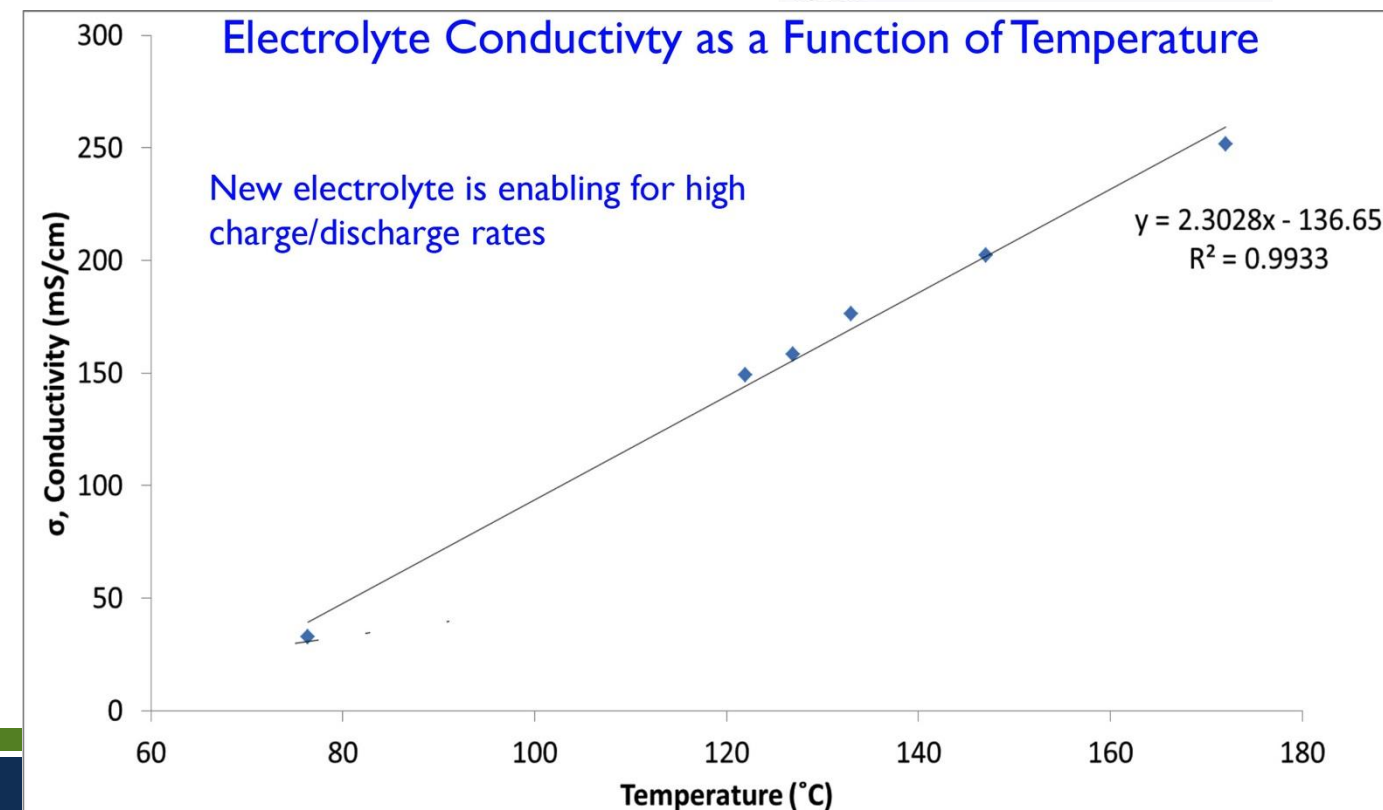
Iodine Cell Chemistry

Anode	$\text{Na} = \text{Na}^+ + e^-$	$E_0 = -2.71\text{V}$
Cathode	$2\text{I}^- = \text{I}_2 + 2e^-$	$E_0 = 0.54\text{V}$
Overall	$2\text{Na}^+ + 2\text{I}^- = 2\text{Na} + \text{I}_2$	$E_0 = 3.25\text{V}$

- We continued to increase the cell size, and we have developed, and are currently using 20 Wh cells
- have developed a new iodine catholyte that has high conductivity (0.2 S/cm at 150 ° C) and we believe will enable high charge and discharge rates - 50 mA/cm²
 - The solvent system is stable in contact with iodine
 - The high discharge rate will reduce the cost of power



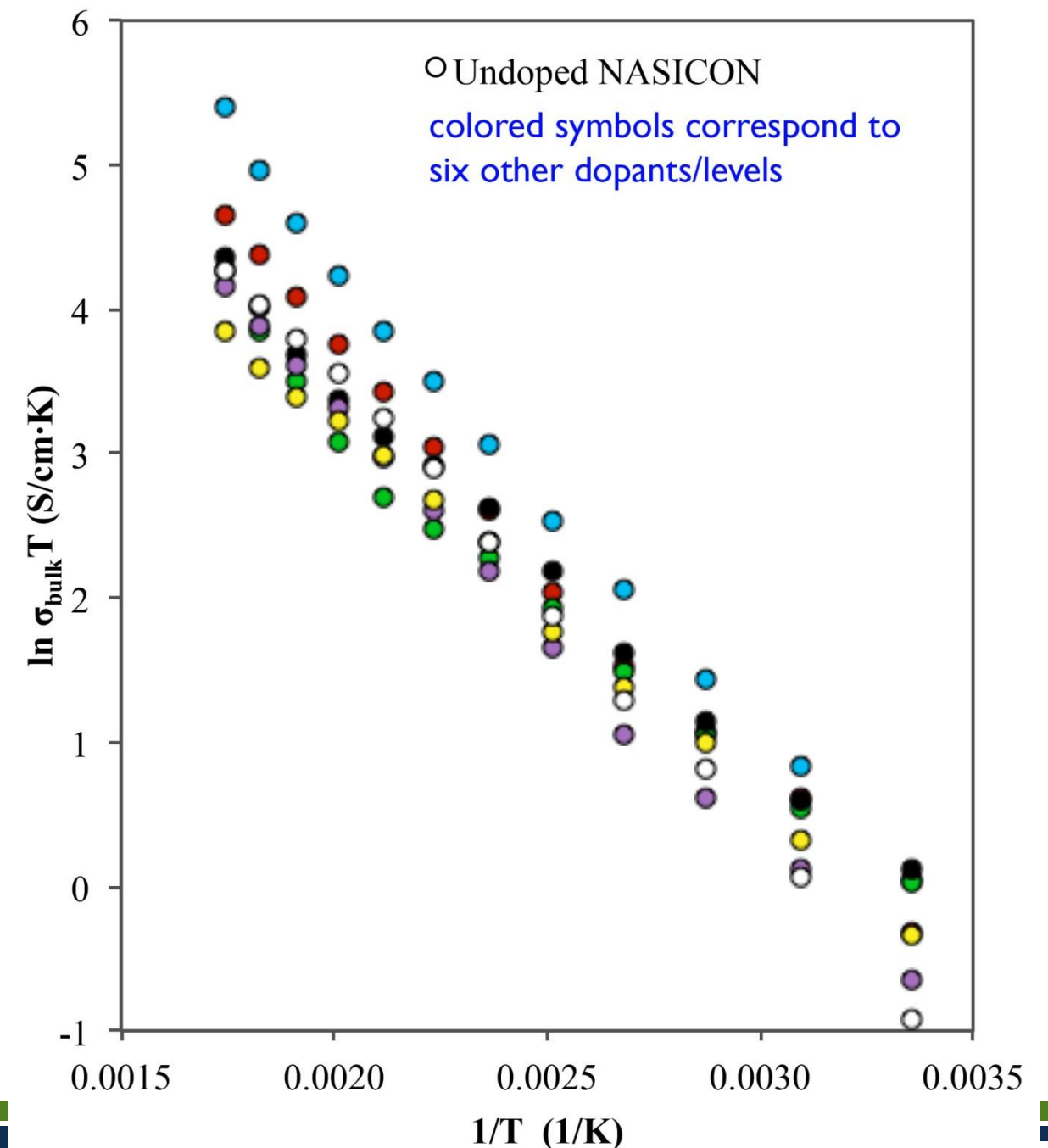
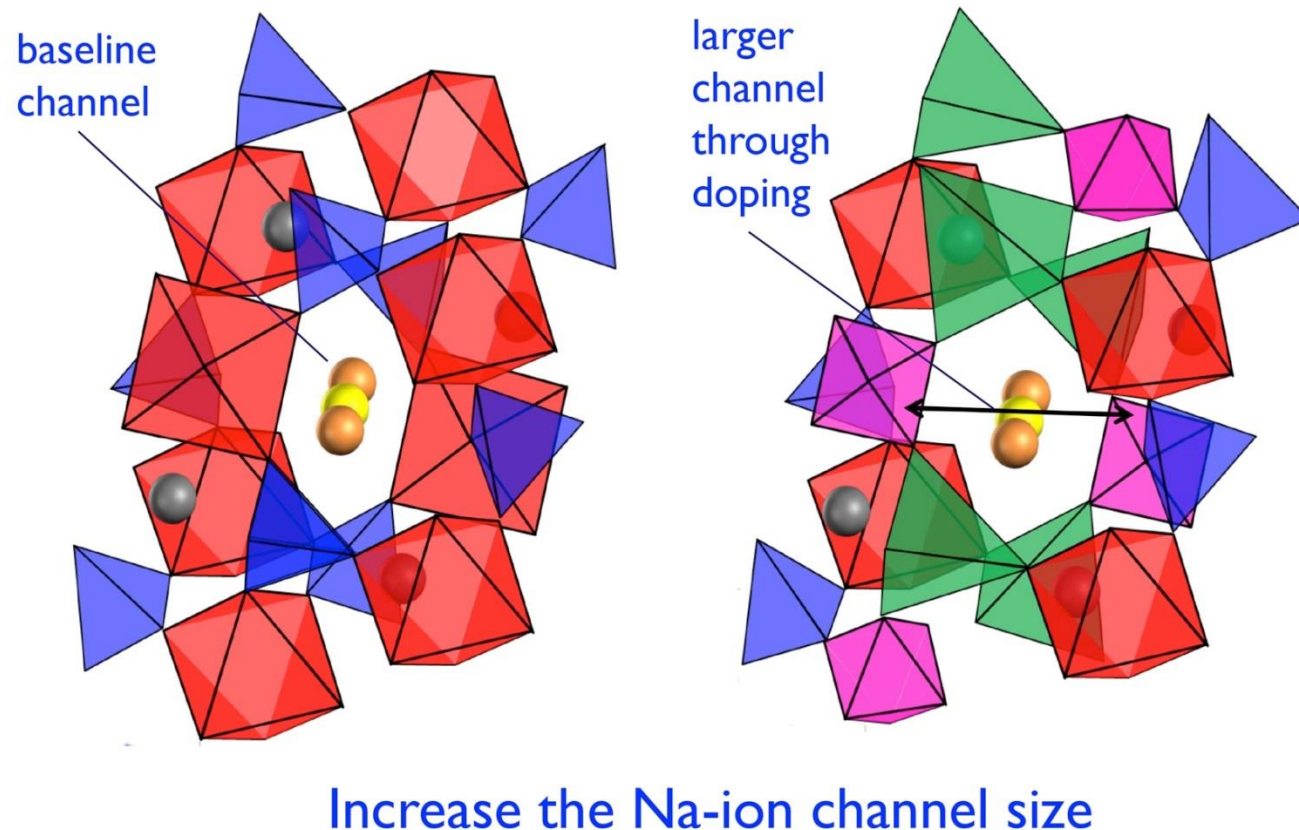
The results obtained in the laboratory prototypes, as well as the design changes resulting from their use, lead to development of the conceptual design for the large-sized system



Improving the conductivity of NaSICON through doping

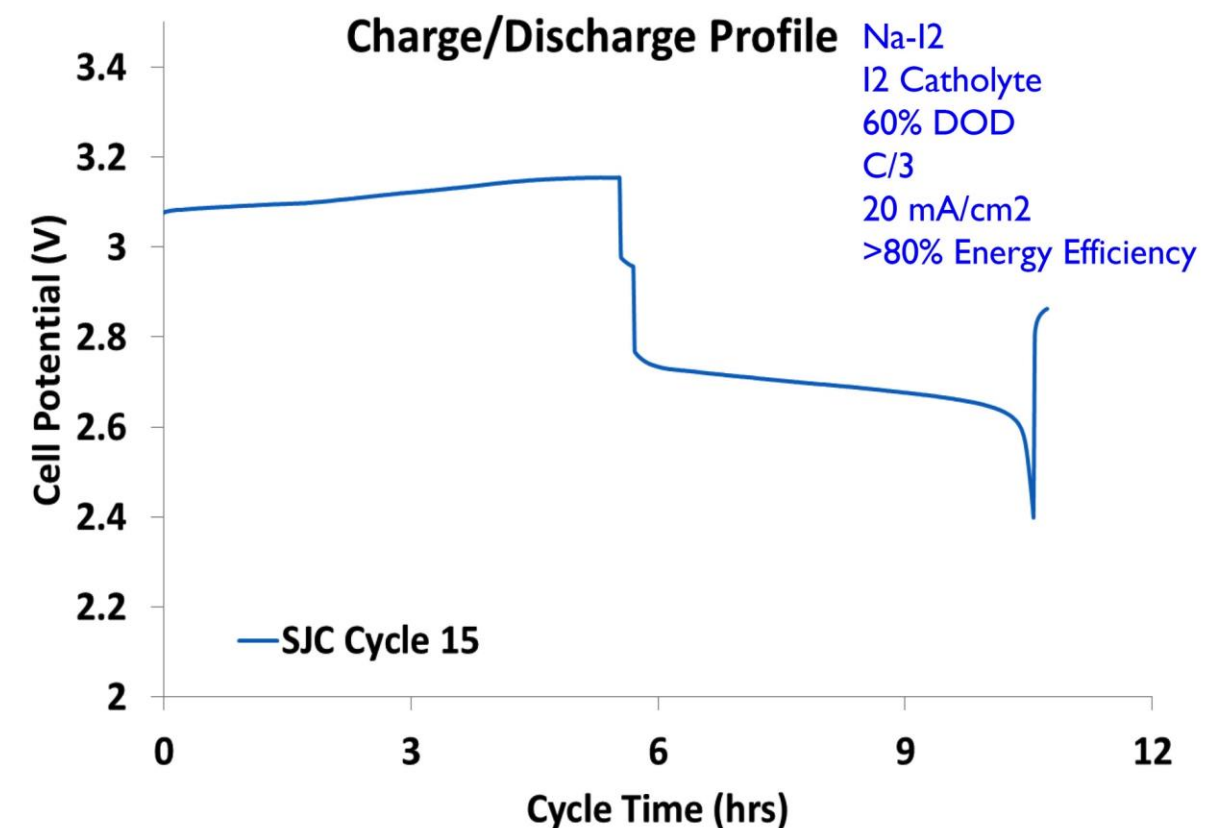
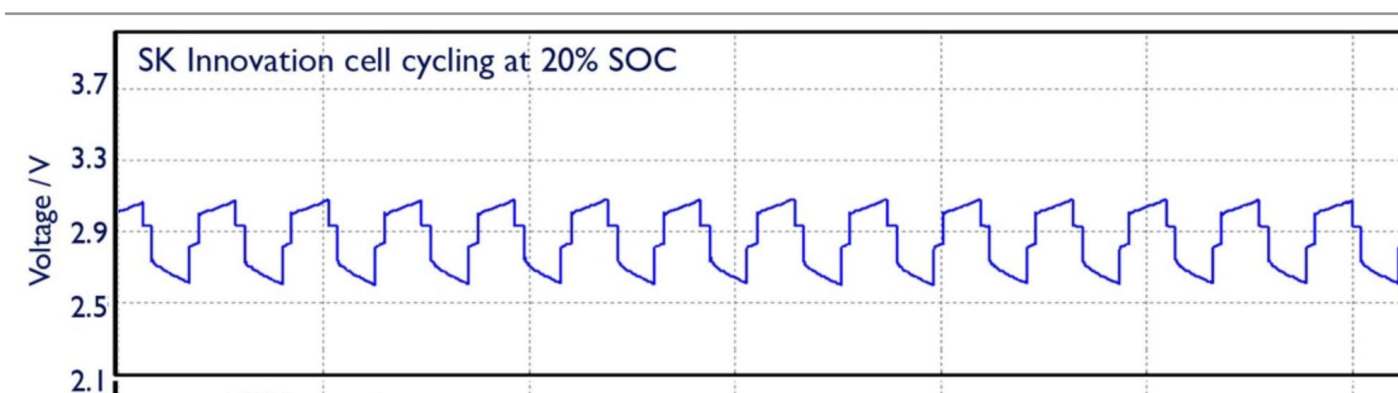
- Improve cell performance by increasing the conductivity of NaSICON
 - aliovalent doping of the Zr^{4+} site.
- NASICON was doped with both +3 and +2 oxidation state cations
- The doping level was adjusted to maintain high purity of NaSICON

- Dopant composition has a significant effect on conductivity – a **3X increase** in conductivity over undoped NaSICON for a select dopant and level:
- $3.75 \times 10^{-3} \text{ S/cm}$ vs. $1.34 \times 10^{-3} \text{ S/cm}$ at 25°C



Cell Performance

- Cell details
 - Temperature = 120 °C
 - Anode: molten Na
 - Cathode: I₂ based catholyte
- The cell exhibits a nominal open circuit voltage (OCV) of 2.95 V and is different from theoretical
 - determined that other iodide species (I₃⁻) are active, not just iodine (I₂), leading to slightly lower cell voltages
- 85% energy efficiency of current design
 - Cell being redesigned to reduce ohmic loss
 - cell is being redesigned to eliminate loss of I₂
- Demonstrated over 300 charge/discharge cycles
- Currently Scaling-up cell size to 100 Wh



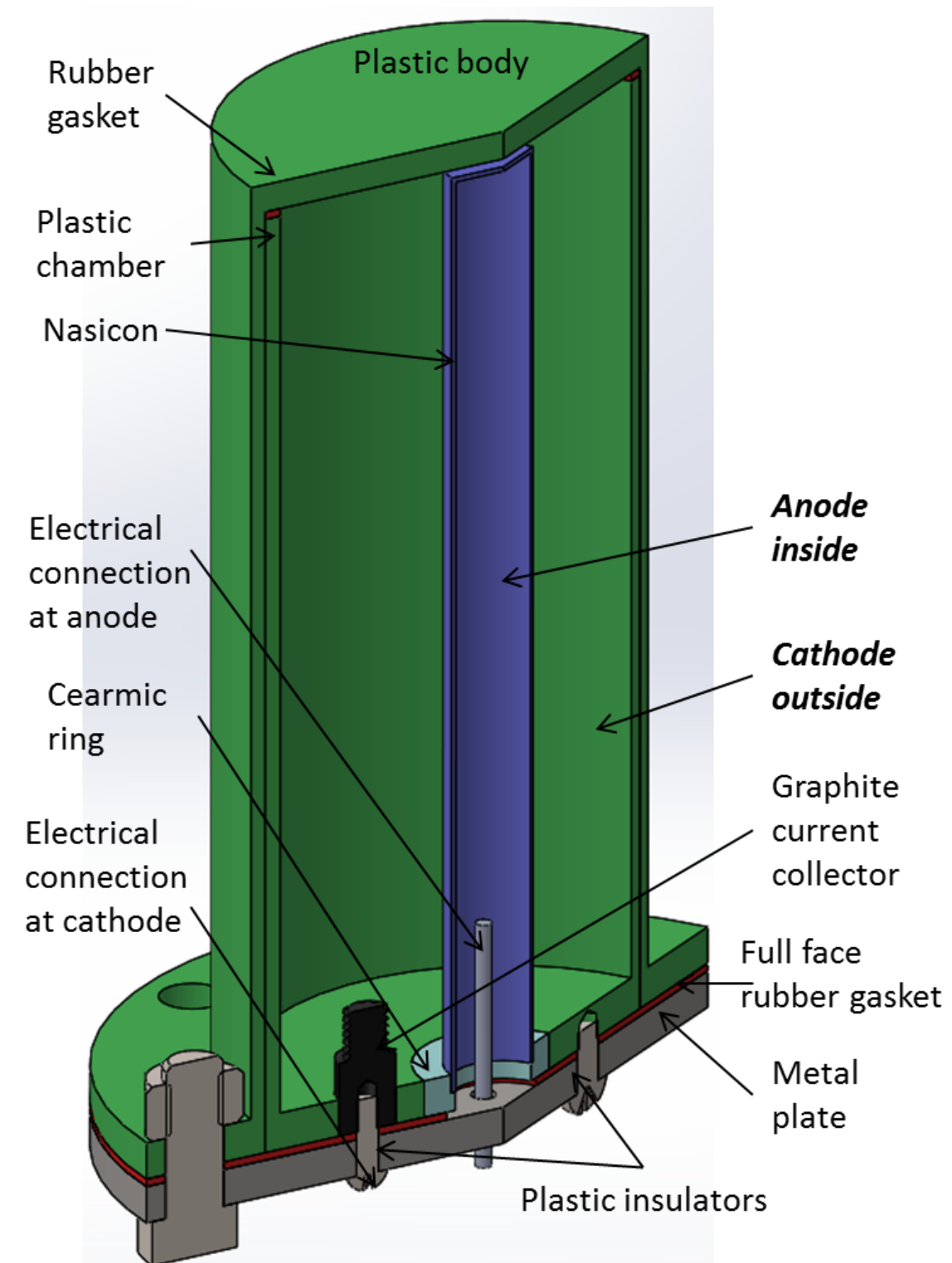
100 Wh Conceptual Design

Enough information is now available to develop a conceptual design for a large-scale system, and project the cost and safety basis

- 100 Wh conceptual design currently being fabricated
- 100 Wh cell used to develop cost basis projections
 - The low operating temperatures allow use of low cost cell materials – e.g. plastics
 - I_2 vapor pressure: 0.26 atm @ 120 C
- Design being used to develop preliminary safety basis

For the cost basis, we have:

- Determined materials mass balance unit cell dimensions
 - For 100 Wh capacity
- Defined cylindrical geometry with w/Na inside NaSICON tube
- Assumed electrochemical performance parameters from 25 Wh cell
 - Basic condition: NaI solid in the porous felt cathode for catholyte
 - Capacity utilization ~ 90% theoretical
 - Average voltage, SOC range etc.
 - Note: Unit cell performance @ 100 Wh not yet determined
- Identified critical parameters that effect the cost (\$/kWh)
 - Raw material costs
 - NaSICON membrane
 - CAPEX (Capital Expenditure) Equipment List & Pricing
 - Battery materials, unit cells and modules production labor costs
 - Electricity & etc. (utilities)



Projected Cost Basis

- Cost estimates developed for both the cell- and module-levels, which includes all relevant items such as floor loss, bus bars/interconnects, power conditioning, capital cost expenditures, etc
- Estimates were developed for best, worst, and intermediate case conditions
 - conditions adjusted to account for each, such as floor loss ranging from 12% (worst case) to 6% best case))
- Raw material costs constitute approximately 35% of the overall cost
 - Iodine accounts for approximately 88% of these costs corresponding to $\approx 31\%$ of total cost
 - sodium is 1%
- The 100 \$/kWh goal is achievable under the optimistic case conditions

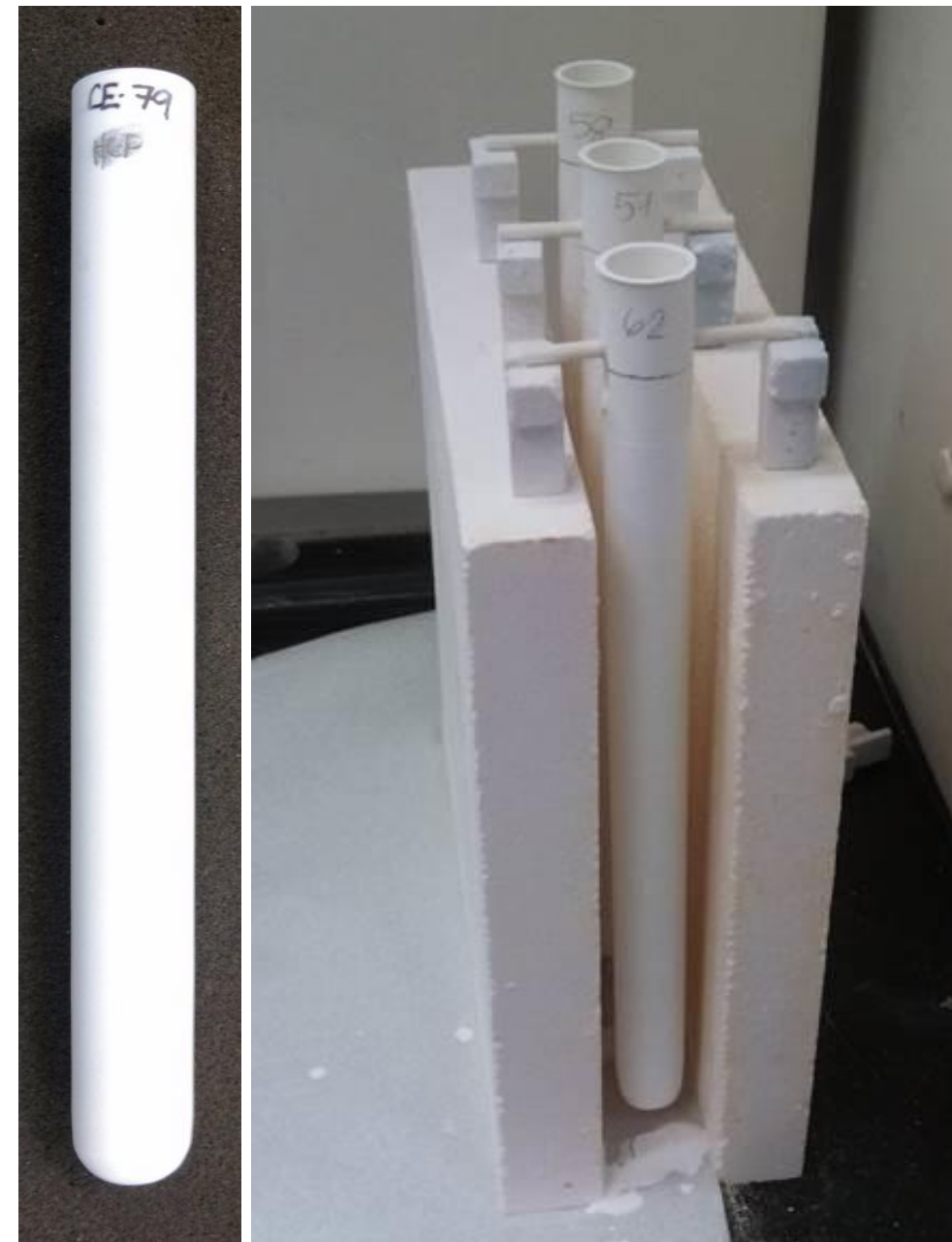
Unit Cell Projections	Value
Cell capacity	100Wh
NaSICON Dimensions	0.9" x 8"
C-rate	C/5
Current density (mA/cm ²)	51.9
Cathode volume	153.7
Usable NaSICON Surface Area	115.6 cm ²
Cathode Thickness (cm)	1.51
Cell volume	306.4
Cell dimension (Φ /cm x L/cm)	4.26 x 21.5
Vol E/D(Wh/L)	326.3
Electrolyte Volume(mL)	80.9
Electrolyte Weight(g)	202.39
Specific Energy (Wh/kg)	193
Energy Density (Wh/l)	326

I ₂ Cost Estimate	\$/MT
Worst Case	41,000
Probable	24,000
Best Case	12,000

Projected Cost	Worst Case (\$/kWh)	Probable (\$/kWh)	Best Case (\$/kWh)
Unit Cell	231.3	146.3	89.0
Module	267.3	175.3	111.0

NaSICON Thimble Tube Production

- Conceptual design and cost estimates are predicated on the availability of large-size NaSICON tubes
- Ceramtec is developing the capability to commercialize the production process of closed-ended tubes for the 100 Wh cell configuration (This activity is supported solely by Ceramtec.)
- Adopted Cold Isostatic Pressing method as the commercial production process
 - have been successful in fabricating near net shape closed ended tubes
 - tube dimension: 8.25"x 0.905"x 0.055"
- Ceramtec is also developing other geometries, such as flat plates
- We have considered the flat plate configuration for use in a bipolar battery design, but have opted NOT to use it at this time
 - in the event of a single cell failure, an entire module must be serviced/replaced
 - from a safety perspective, it is possible that a single point failure in one cell might lead to a cascading module/battery failure with unfortunate results



Projected Safety Basis of the Na-I₂ System

Safety is a an important consideration in regard to deployment of energy storage systems of any type.



Image Source: WindPower Monthly
<http://www.windpowermonthly.com/article/1284038/analysis-first-wind-project-avoids-storage-30m-fire>

- Many factors must be considered when designing and evaluating the safety characteristics of a storage system
 - size of the system
 - chemistry of the system
 - response of the system to abnormal events
 - proximity to population centers
 - credible abnormal event scenarios
 - approach for dealing with abnormal events
 - neighbors
 - etc
- So many factors must be considered, that it is impractical to conduct tests to evaluate all possible credible events

It may not be practical to conduct tests to evaluate all possible credible events

- Our Approach:
 1. chemical and engineering experience and intuition
 2. develop a validated computational tool that can predict behavior
 - Leverage the significant investments that the Department of Energy has made at SNL in Advanced Scientific Computing (ASC) for Science-based Stockpile Stewardship, and adapt the code to energy storage safety analysis

Leveraging the ASC Investments to Battery Safety in Abnormal and Thermal Environments

SNL has developed simulation tools that predict thermal environments and the response of the object to that environment. These have been validated!

Can predict:

- Turbulent fluid mechanics (buoyant plumes)
- Participating Media Radiation (PMR)
- Reacting flow (hydrocarbon, particles, solids)
- Conjugate Heat Transfer (CHT)

Multiphysics Coupling

(the equations and couplings)...

Fluid/PMR

Fluids:

$$\frac{\partial \bar{\rho} \tilde{h}}{\partial t} + \frac{\partial}{\partial x_j} \bar{\rho} \tilde{h} \tilde{u}_j = - \frac{\partial}{\partial x_j} (\bar{q}_j + \tau_{hu_j}) - \frac{\partial \bar{q}_i^r}{\partial x_i} + \frac{\partial P}{\partial t} + \tilde{u}_j \frac{\partial P}{\partial x_j} + \tau_{ij} \frac{\partial u_i}{\partial x_j}$$

RTE:

$$s_j \frac{\partial}{\partial x_j} I(\vec{r}, s) + (\bar{\mu}_a + \bar{\mu}_s) I(\vec{r}, s) = \bar{\mu}_a I_b + \mu_s \frac{G}{4\pi}$$

Coupling:

$$\frac{\partial \bar{q}_i^r}{\partial x_i} = \mu_a [4I_b - G(\vec{r})]$$

Fluid/Thermal

Fluids:

$$\frac{\partial \bar{\rho} \tilde{h}}{\partial t} + \frac{\partial}{\partial x_j} \bar{\rho} \tilde{h} \tilde{u}_j = - \frac{\partial}{\partial x_j} (\bar{q}_j + \tau_{hu_j}) - \frac{\partial \bar{q}_i^r}{\partial x_i} + \frac{\partial P}{\partial t} + \tilde{u}_j \frac{\partial P}{\partial x_j} + \tau_{ij} \frac{\partial u_i}{\partial x_j}$$

Thermal:

$$\rho C_P \frac{\partial T}{\partial t} + \frac{\partial}{\partial x_j} q_j = S_T$$

Coupling:

$$q_j^s n_j^s = q_j^f n_j^f$$

PMR/Thermal

RTE:

$$s_j \frac{\partial}{\partial x_j} I(\vec{r}, s) + (\bar{\mu}_a + \bar{\mu}_s) I(\vec{r}, s) = \bar{\mu}_a I_b + \mu_s \frac{G}{4\pi}$$

Thermal:

$$\rho C_P \frac{\partial T}{\partial t} + \frac{\partial}{\partial x_j} q_j = S_T$$

Coupling:

$$q_j^s n_j^s = q_j^R n_j^R$$

ASC for Safety Basis Predictions

- Specific Objective:
 - Predict the safety basis of the Na–I₂ battery
- Long Range Goal:
 - Develop a computational tool that can be used to predict the safety basis of any storage system
- When successful, this tool can be used by
 - developers
 - first responders
 - siting review panels
 - building A&E design
 - government entities
 - regulators
 - other stakeholders

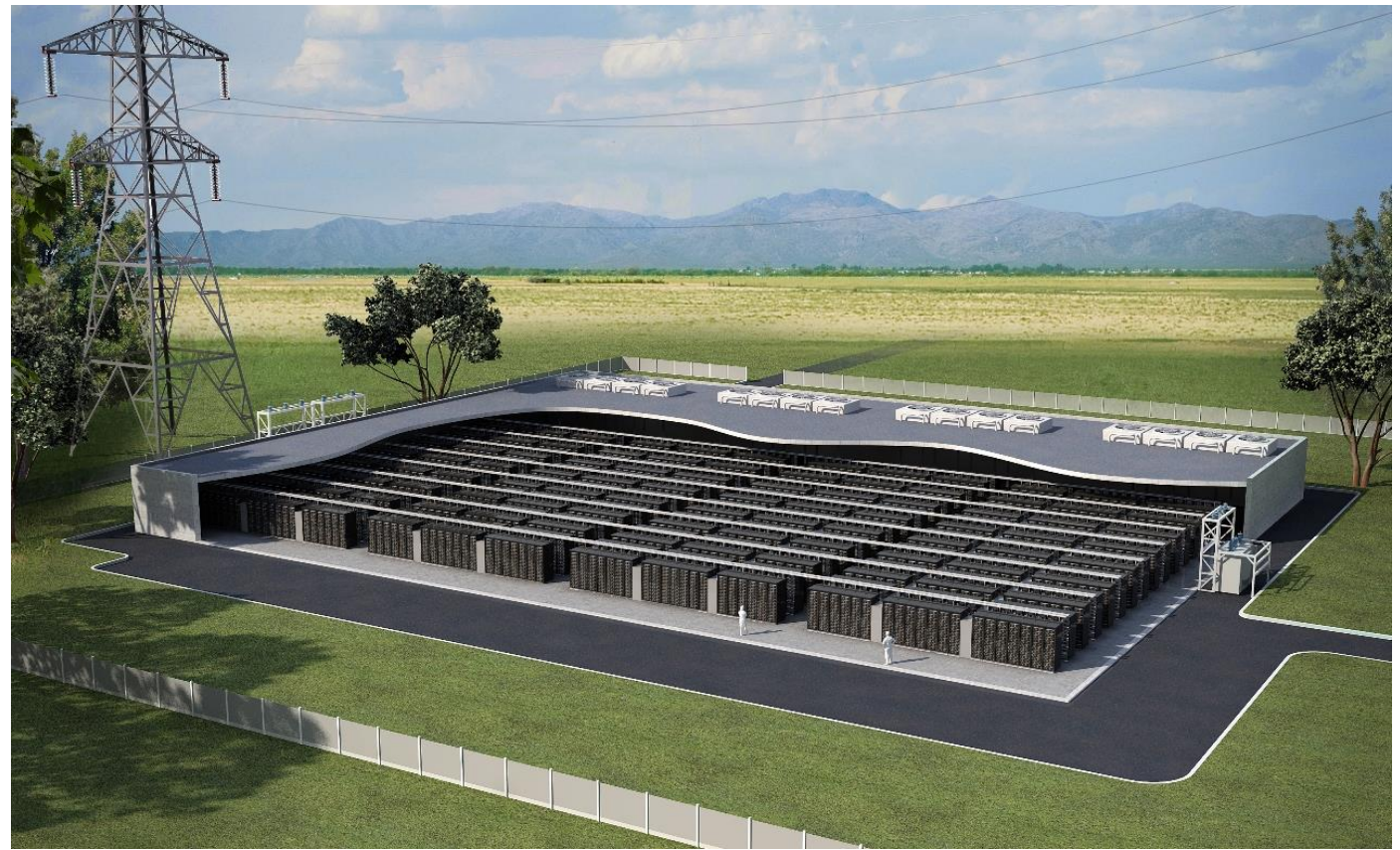
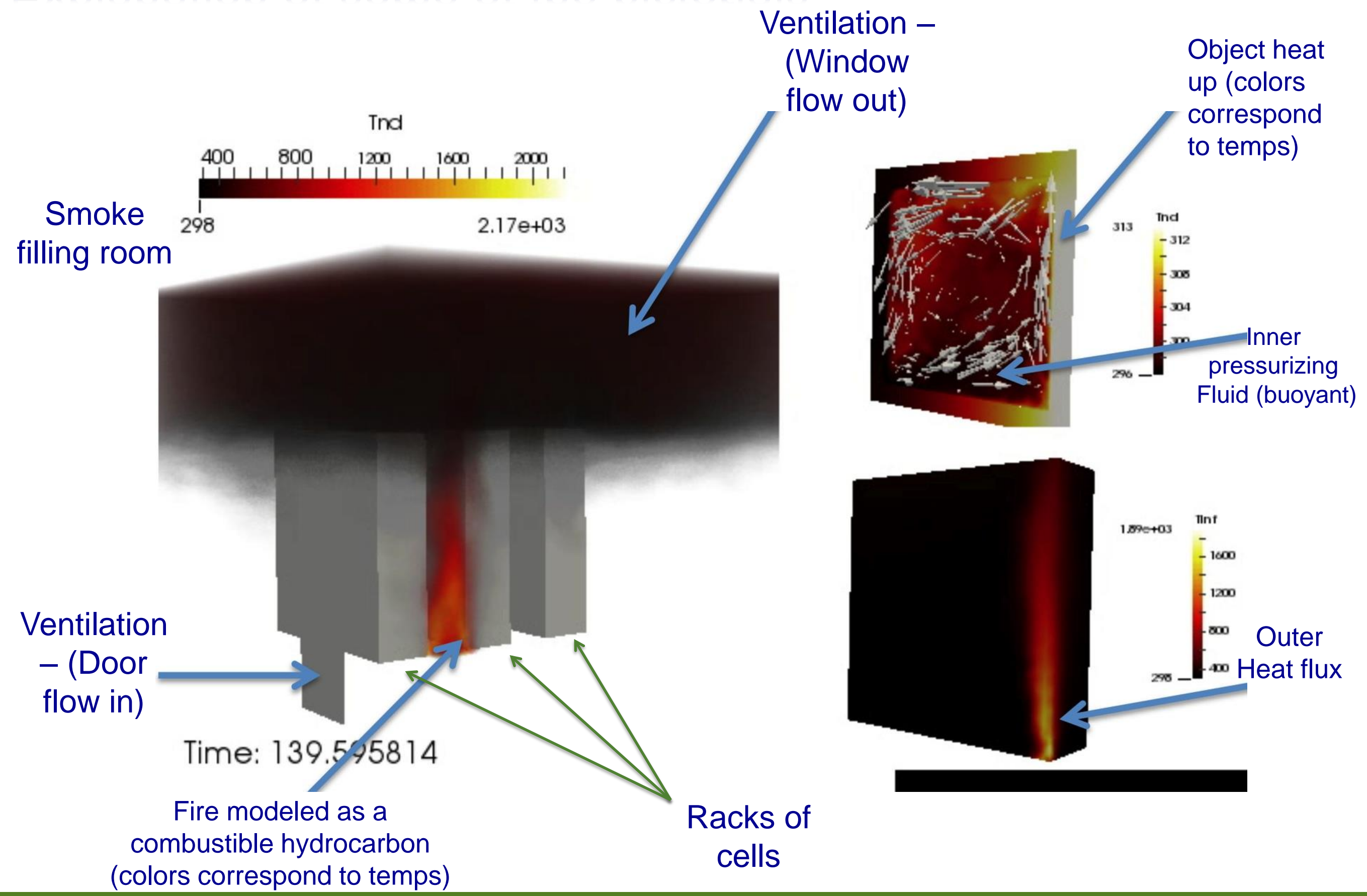


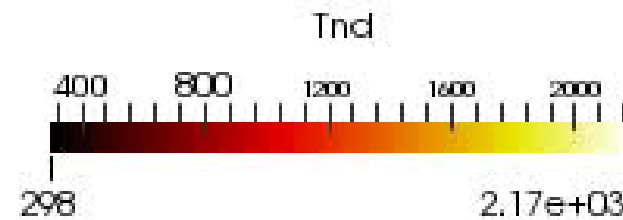
image source: Silicon Valley Innovation Center,
<http://www.svicenter.com/business/disruptive-innovations-energy-storage/>

Explanation of some of the pictorials

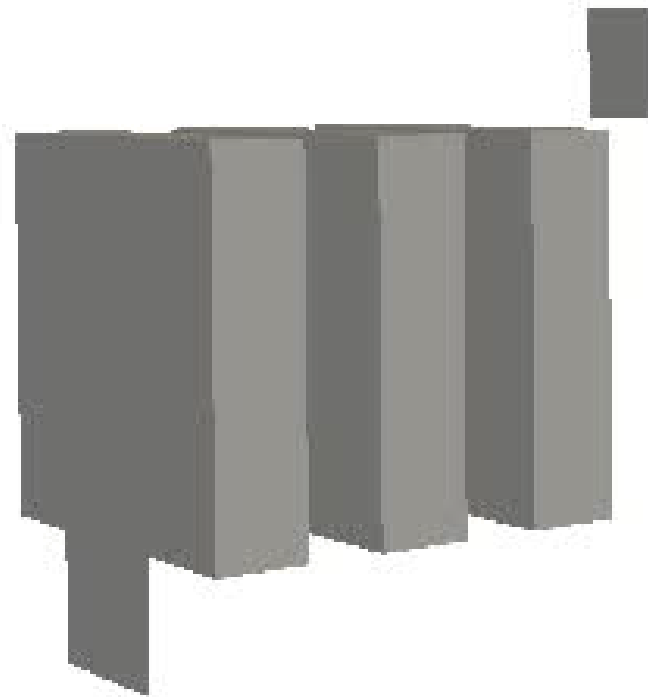


Thermal environment (No ventilation)

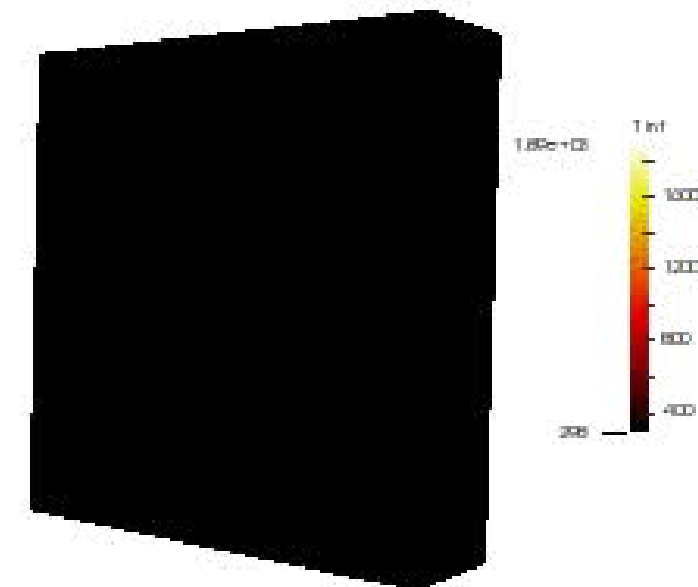
- Can predict spatial-temporal-thermal characteristics of an event
- Can predict spatial-temporal-thermal characteristics for nearest neighbors, next nearest neighbors, etc
- Can predict internal pressures, compositions, concentrations,



Adjacent racks of batteries in a building with a door and vent and a heat source between the battery racks. There is a door on the left, and a window up high on the right. *No forced ventilation in room.*



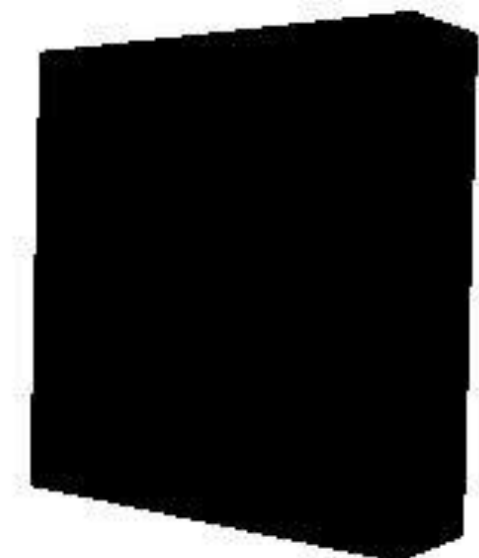
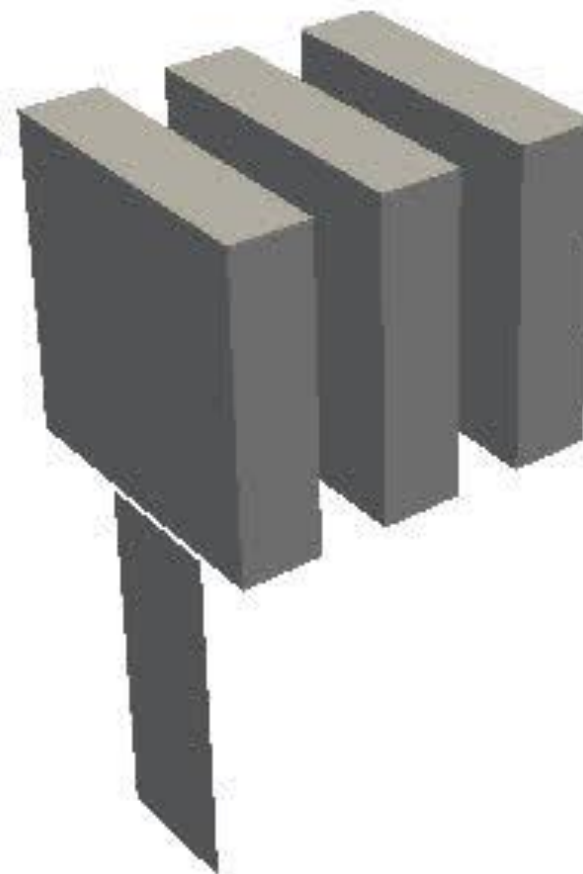
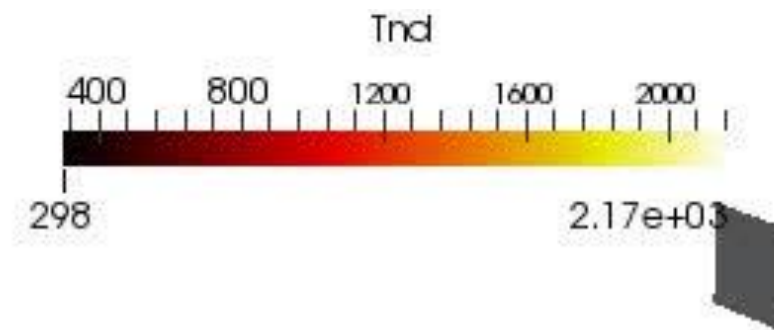
Time: 0.000000



Model allows inclusion of environmental factors

- can predict building design characteristics on the spatial-temporal-thermal behavior during event
 - ventilation and ventilation rate
 - location of ventilation
 - room size
 - stack locations
 - etc.

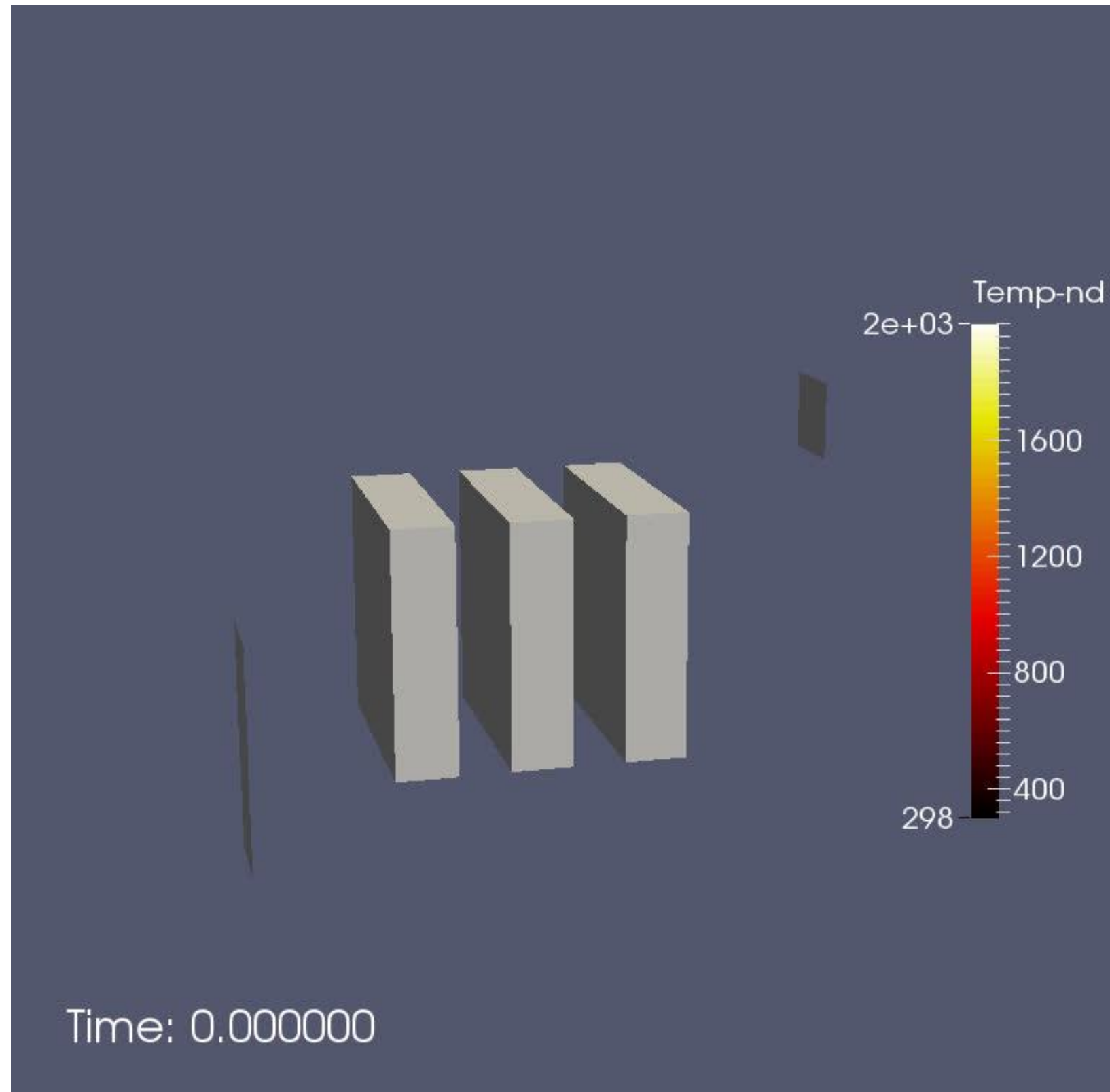
High Ventilation



Time: 0.000000

Model allows evaluation of suppression technologies

- This movie predicts water as a suppressant, but other suppressants can also be simulated
 - CO₂, halocarbons, etc

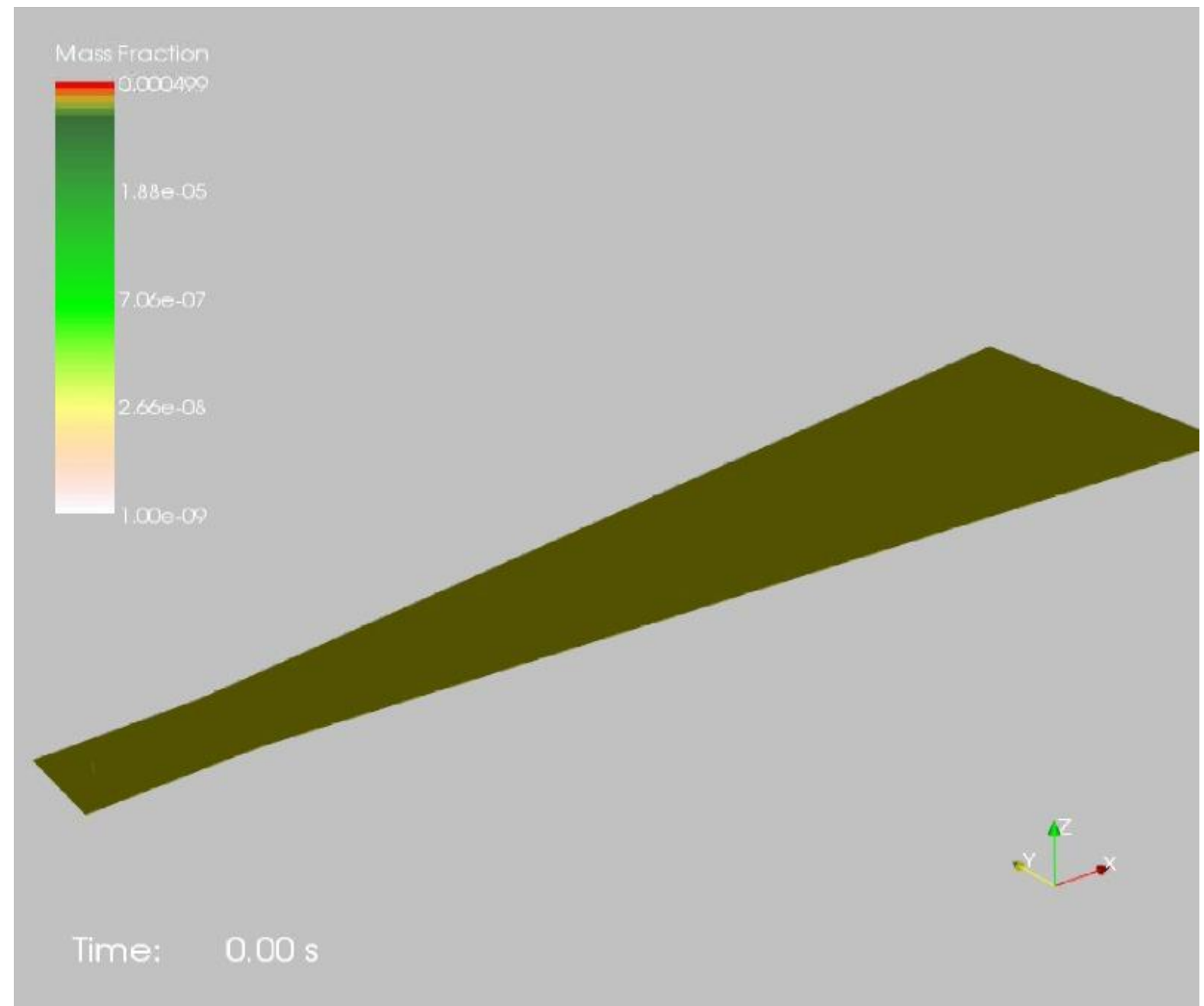


Point Source Emission Prediction

- Can predict spatial-temporal-concentration of chemical species from a point source
- Can predict chemical composition of effluent (not shown)
- May be able to predict surface contamination post event to aid in cleanup

Colors represent to concentrations (mass fraction)

Model incorporates prevailing wind conditions around source



FY14 accomplishments

- Doping to improve conduction in NaSICON has been demonstrated (3X increase has been shown)
- A new iodine catholyte having high conductivity has been developed allowing “low” temperature operation (200 mS/cm at 120 C)
- 25 Wh cell shows good performance, scale-up in process
- A conceptual design large-scale cell has been developed (100 Wh cell)
- A “best” case levelized cost of energy has been estimated
 - cell level - 89 \$/ kWh
 - module level – 111 \$/ kWh
- Completed the initial stages of predictive battery safety mod-sim tool
 - Potential for widespread applicability beyond battery design itself
 - Have presented to the interagency lithium battery safety group, and are in discussions about tool use for: 1) battery certification; and 2) building design
 - Adaptable to safety design of multiple battery chemistries
 - Considers total chemical energy, fire and cascading reaction events
 - Goal: “safe by design” battery chemistries and grid-scale systems

Future Tasks

- Demonstrate performance at the 100 Wh cell-level
- Refine/update cost basis
- Develop cost basis for power - \$/kW
- Continue development of the predictive safety tool for the Na-I₂ system.

Publications & Patents

PUBLICATIONS

1. “Optical measurements of impurities in room-temperature ionic liquids”, Jason M. Porter, Christopher B. Dreyer, David Bicknase, Shubham Vyas, C. Mark Maupin, Joe Poshusta, Jerry Martin; J. Quantitative Spectroscopy & Radiative Transfer, in press.
2. “Computational model of a sodium–copper-iodide rechargeable battery,” H. Zhu, S. Bhavaraju, and R. Kee, *Electrochimica Acta* (2013), <http://dx.doi.org/10.1016/j.electacta.2013.09.010>
3. “Higher Conductivity NASICON Electrolyte for Room Temperature Solid-State Sodium Ion Batteries” G.T. Hitz, K.T. Lee, and E.D. Wachsman, *Nature Communications*, submitted
4. “Highly Li-Stuffed Garnet-Type Structured $\text{Li}_{7+x}\text{La}_3\text{Zr}_{2-x}\text{Y}_x\text{O}_{12}$ ” G.T. Hitz, E.D. Wachsman, and V. Thangadurai, *J. Electrochem. Soc.*, 160, A1248-A1255, (2013).
5. N.S. Bell, C. Edney, D. Ingersoll, and E.D. Spörke, “The Influences of Excess Sodium on Low Temperature NaSICON Synthesis,” *J. Mater. Chem.* 2013; submitted for publication

PATENT APPLICATIONS

1. “Higher Conductivity NaSICON Electrolyte for Room Temperature Solid-State Sodium Ion Batteries,” E.D. Wachsman, G.T. Hitz, and K.T. Lee, Filed September 25, 2012, U.S. Patent Application Serial No. 61/705,352
2. “Moderate temperature sodium battery”
3. “Battery with non-porous alkali metal ion conductive honeycomb structure separator”
4. “Sodium-Halogen Battery”, Provisional 61/697,608, Filed Sep 6, 2012 (Filed as full patent on Sep 6, 2013)
5. “Battery with bromine or bromide electrode and sodium selective membrane”, 61/736,444, Filed Dec 12, 2012
6. “Sodium-halogen secondary cell”, Provisional 61/777,967, Filed Mar 12, 2013, (Published: US20140065456)
7. “Sodium-halogen secondary flow cell”, Provisional 61/781,530, Filed March 14, 2013
8. “NaSICON membrane based Na-I₂ battery”, Provisional 61/888,933, Filed 9 October 2013
9. Sodium-Halogen Molten Salt Battery, Provisional filed, 2014

Thank You to the DOE OE and especially Dr. I. Gyuk for his dedication and support to the ES industry and Sandia's ES Program.



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Questions?

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Backup Slides

The current modeling effort supports laboratory-scale Na-I battery

